

# Phase behavior of repulsive polymer-tethered colloids

Behnaz Bozorgui, Maya Sen, William L. Miller, Josep C. Pàmies and Angelo Cacciuto\*

*Department of Chemistry,  
Columbia University, 3000 Broadway,  
New York, New York 10027*

(Dated: January 21, 2010)

We report molecular dynamics simulations of a system of repulsive, polymer-tethered colloidal particles. We use an explicit polymer model to explore how the length and the behavior of the polymer (ideal or self-avoiding) affect the ability of the particles to organize into ordered structures when the system is compressed to moderate volume fractions. We find a variety of different phases whose origin can be explained in terms of the configurational entropy of polymers and colloids. Finally, we discuss and compare our results to those obtained for similar systems using simplified coarse-grained polymer models, and set the limits of their applicability.

## I. INTRODUCTION

Understanding how colloidal particles spontaneously organize into ordered macroscopic aggregates is a long-standing challenge that has recently acquired an extra degree of complexity. In fact, advances in particle synthesis [1–5] have opened the way to the production of colloidal particles that are anisotropic both in shape and surface chemistry. This provides an unlimited number of building blocks that can spontaneously assemble into an unprecedented variety of structures with potentially novel functional, mechanical, and optical properties.

The effect of the anisotropy of nanoparticles on their macroscopic ordering can be addressed in terms of (a) the form of the inter-particle interaction, and (b) their shape. Not surprisingly, for both cases there is ample evidence (see for example [6–15] and references therein) of a strong correlation between the physical properties of the components and those of the resulting aggregates. This phenomenology must be thoroughly explored as it may lead the way to a rational design of the components to target desired macroscopic structures.

Here we focus on the role of particle shape. Specifically, we study the phase behavior of a particularly interesting class of deformable particles that is obtained by grafting a single long chain to a each colloid. What makes this hybrid colloid intriguing is that, because of the flexibility of the polymer, the overall shape of the particle is not fixed, but can be spontaneously altered depending on the specific thermodynamic states imposed on the system. A few experimental realizations of particles compatible with our model have recently been synthesized [16–18]. The dual nature of these nanoparticles may open the door to exotic self-assembled structures that are not typically seen in systems of nanoparticles with intrinsic (invariable) shape, and its key elements are very similar to those of asymmetric diblock copolymers.

Unlike recent experimental and theoretical studies on particles coated with dsDNA, which can form com-

plex networks between the particles via linker-mediated dsDNA-dsDNA interactions[19–21], no explicit attractive forces are introduced in our system. As a result, any phase described in this paper will be mostly driven by a nontrivial balance between the configurational entropy of the colloids and that of the chains.

In this paper we use molecular dynamics simulations to understand the phase behavior of a system of repulsive, polymer-tethered colloidal particles. Specifically, we consider a system in which each colloid is connected to one of the end groups of a single polymer, and we study how different structures emerge depending on the polymer length. Furthermore, we explicitly analyze both the case of ideal and self-avoiding polymers.

Capone *et al.* [22] have recently analyzed the phase behavior of model of di-block copolymers. Their study bears similarities with our work, as some of the self-assembled structures are common to both systems. However, the two systems differ in the way the polymers are modeled. Here we use an explicit beads-and-springs model, while spheres with a soft potential were employed by Capone *et al.* Though computationally expensive, our model enables us to gain a detailed understanding of the mechanisms behind the nontrivial phase behavior emerging in this system, and this choice will turn out to be quite critical when considering the case of non-ideal polymers. To the best of our knowledge this is the first computational study that explicitly accounts for the internal degrees of freedom of the polymer for this particular system.

## II. MODEL

We model the polymer-tethered colloids as a polymer of  $N + 1$  monomers, with  $N$  monomers of diameter  $\sigma_1$ , and monomer  $N + 1$ , representing the colloidal particle, of diameter  $\sigma_2$ . See Fig. 1 for a depiction of the particle. In this model the  $N^{th}$  monomer is not constrained to be at a specific location on the surface of the colloid, but can freely diffuse on it; constraining this monomer would yield the same equilibrium properties.

Excluded volume interactions between any two par-

---

\*Electronic address: ac2822@columbia.edu

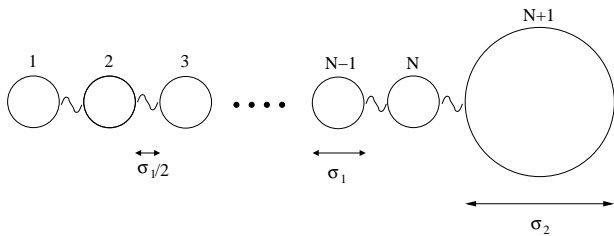


FIG. 1: Schematic representation of our model for a hybrid, polymer-grafted colloid. The first  $N$  monomers of diameter  $\sigma_1$  represent the chain, whereas the  $N + 1^{\text{st}}$  monomer of diameter  $\sigma_2$  represents the colloidal particle. Both particles are assumed to have equal mass.

ticles in the system are enforced via a purely repulsive shifted-truncated Lennard-Jones potential

$$U_{i,j}^E(r) = \epsilon_{i,j} \left[ \left( \frac{\sigma_{i,j}}{r_{i,j}} \right)^{12} - \left( \frac{\sigma_{i,j}}{r_{i,j}} \right)^6 + \frac{1}{4} \right], \quad \forall r_{i,j} \leq 2^{1/6} \sigma_{i,j} \quad (1)$$

The indices  $i, j \in \{1, 2\}$  indicate the identity of the particle (polymer or colloid, respectively.)  $\sigma_{i,j} \equiv (\sigma_1 + \sigma_2)/2$ .  $r_{i,j}$  is the distance between the centers of mass of any two particles. Finally,  $\epsilon_{i,j} = 10k_B T \forall i, j$  when considering self-avoiding polymers, and we set  $\epsilon_{1,1} = 0k_B T$  for the case of ideal polymers.

In each hybrid colloid, particles are linearly connected via the harmonic spring potential

$$U_{i,i+1}^S = k_s (r_{i,i+1} - r_{i,i+1}^0)^2 \quad (2)$$

where  $k_s = 150k_B T$  is the spring constant, and  $r_{i,i+1}^0 = \sigma_{i,i+1} + \sigma_1/2$  is the equilibrium distance.

We perform  $NPT$  molecular dynamics simulations using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [23]. Pressure and temperature are kept constant by means of a Nosé-Hoover thermostat [24] and barostat [25] with additional drag terms, with coefficients  $\xi_T = 1\tau_0^{-1}$  and  $\xi_P = 1\tau_0^{-1}$  respectively ( $\tau_0$  is the reduced time unit), to damp the dynamics and suppress large temperature and pressure oscillations.

The simulation box is a cuboid with periodic boundary conditions and, for pressure control, we use decoupled box lengths in each of the three Cartesian coordinates. This allows box aspect ratios to vary slightly to accommodate crystalline structures.

The system initial configurations are prepared by performing  $NVT$  simulations in the gas phase. Once the system is equilibrated, and the initial pressure  $P_0$  is extracted from the thermalized configurations, we slowly ramp the pressure to the desired value  $P_1$  starting from  $P_0$  (all pressures referred in this paper are rescaled with respect to the colloidal interaction energy  $\epsilon_{22}$  and the colloidal diameter  $\sigma_2$ ). Each subsequent simulation performed at a constant pressure  $P_i$  starts from the thermalized configuration at pressure  $P_{i-1}$  ( $P_{i-1} < P_i$ ). The

dimensionless  $\Delta P$  was typically set to 0.01, and was refined or extended depending on the distance from the transition point. This procedure ensures that the chains have the time to fully equilibrate. The relatively short chain lengths considered in this study, and the relative low densities at which most of the phases occur, result in a system that does not have a pathological dynamical behavior. Therefore, the very slow pressure annealing described above, together with the monitoring of all the observables considered in this study, including the average cluster size and its distribution where sufficient to establish equilibrium. Moreover, we checked that we could reproduce all the phases starting from completely different initial configurations.

In our study we considered tethers with a minimum of  $N = 5$  and a maximum of  $N = 300$  monomers, and colloids of diameter ranging from  $\sigma_2 = 2\sigma_1$  to  $\sigma_2 = 18\sigma_1$ .

All of our simulations are carried out using a total of 512 hybrid colloids at room temperature, and the longest simulations took about six months of computer time on an Intel Xeon X5355 2.66GHz processor. In all simulations we set the time step to  $\Delta t = 0.015\tau_0$ . For each pressure annealing step,  $\Delta P$ , simulations were run for a minimum of  $10^6$  (for the small chains) to a maximum of  $10^8$  timesteps (for the long chains.)

Every observable reported in this paper is expressed in dimensionless units.

### III. RESULTS

Apart from the harmonic potential, which serves a purely structural purpose by enforcing connectivity between the different components of our hybrid colloid, there are no attractive interactions in our system. As a consequence, the free energy is dominated, at the low concentrations considered in our study, by the configurational entropy of its components. Although the configurational entropy is, strictly speaking, associated with hard potentials, we have chosen a large value for  $k_s$  to ensure that bonds are very close to their equilibrium length, and have also run a few simulations with a stricter excluded volume constraint by setting  $\epsilon_{i,j} = 500k_B T$ . We find no discernible difference between the two cases under several thermodynamic conditions.

What follows are the phase diagrams for ideal and self-avoiding tethers as a function of the volume fraction of colloids,  $\phi \equiv \pi\sigma_2^3 N_c / (6V)$ , and the effective polymer-colloid size ratio, which we define as  $\alpha = 2R_g / \sigma_2$ .  $N_c = 512$  is the number of colloids,  $V$  the volume of the simulation box, and  $R_g$  is the radius of gyration of a polymer tether, which scales as  $R_g \sim (N)^{1/2}$  for ideal polymers and as  $R_g \sim N^{3/5}$  for self-avoiding ones. The calculated bulk prefactors for our models are 0.57 and 0.60 for ideal and self-avoiding chains respectively. Experimentally, one can easily control the behavior of the polymer by altering the properties of the solvent. For instance, the polymer will behave ideally at the solvent

$\theta$  point, and as a SAW at larger temperatures.

### Ideal chains

Figure 2, obtained using several combinations of colloidal radii and chain lengths, shows the different phases arising from the organization of the particles in the system as a function of volume fraction for different values of  $\alpha$ , and presents several interesting features. The lines are a guide to the eye, and are found by identifying the threshold densities and size ratios above which phase change occurred.

For  $\alpha$  sufficiently small,  $\alpha \lesssim 1$ , the presence of the tethers does not alter the ability of the colloids to crystallize into a macroscopic FCC crystal once the system is compressed above a threshold volume fraction. This is exactly how tether-free colloids crystallize under analogous conditions, and is achieved in our system by chain localization into either the interstitial space between the colloids (for very small  $\alpha$ ) or into crystal vacancies as depicted in Fig. 2A. This is only possible as long as the chains are short enough to fit within a vacancy without exerting a significant amount of pressure arising from chain confinement. The formation of crystal vacancies is the first hint of colloidal/polymer segregation. This phase is preceded by a fluid phase of small micelles at a lower volume fraction (Fig. 2 region D). These deform and freeze as the system pressure is increased into structurally FCC-compatible cages: the vacancies in the colloidal crystal lattice. Each vacancy is typically filled by the polymer chains of all colloids surrounding it, and their locations present no obvious translational order. In fact, we find a non-negligible number of vacancy pairs distributed across the colloidal crystal.

Interestingly, for  $1 \lesssim \alpha \lesssim 1.3$ , the colloidal crystal phase ceases to form, and is replaced by a disordered micellar phase (see Fig. 2B). This is clearly due to the increased free energy cost associated with chain confinement into a vacancy which grows quadratically with  $\alpha$ ,  $\Delta F \sim n(2R_g/\sigma_2)^2 = n\alpha^2$ , where  $n$  is the number of chains in the same vacancy. To mitigate this effect, the typical cage sizes become larger and the geometrical rearrangement into an FCC-cell becomes expensive. The presence of these unstructured micelles at large volume fraction frustrates and disrupts the formation of a high density colloidal ordered phase.

Above  $\alpha \sim 1.3$ , the system assembles into low-density micellar crystals (see Fig. 2C, with the colloidal particles freely diffusing at their surfaces. This phase is analogous to that observed using a coarse-grained, soft-sphere model for the polymers [22].

We argue that the dominant contribution to the system pressure in the micellar regime comes from the free energy penalty associated with chain confinement within each micelle. The free energy cost per micelle associated with it can be readily evaluated by simple scaling argu-

ments [26],

$$\Delta f \propto n \left( \frac{R_g}{R_m} \right)^2, \quad (3)$$

where  $R_m$  is the radius of the micelle, from which we estimate that the pressure of the system should scale with micellar radius as

$$P \propto N_m n \frac{R_g^2}{R_m^5}, \quad (4)$$

where  $N_m$  is the number of micelles forming the crystal.

Figure 3 shows how all data collected for different combinations of colloidal radii and polymer lengths in the micellar crystal phase can indeed be collapsed into the same master curve when properly normalized. A power law fit to the data, i.e. the pressure  $P$  imposed in our simulations and the corresponding measured average micellar radius, yields a pressure dependance on  $R_m$ ,  $P \propto R_m^{5.4(2)}$ , which is consistent with the eq. 4 for large values of  $R_m$ . Clearly, our theory breaks down at very large densities, i.e. small micellar radii, where long tethers begin to radiate out of the micellar cores. This happens when the main mechanism of micellar shrinkage involves exclusively colloidal expulsion from the micellar surface, causing significant thickening and layering of colloids in the inter-micellar regions.

Unfortunately extending the validity of our scaling behavior to large size ratios would require performing simulations with very long polymers, and this becomes quickly untreatable. Nevertheless, the fact that all the data gathered in our simulations for different size ratios collapse onto the same master curve is strongly suggestive that the dominant contribution to the system pressure comes indeed from the free energy penalty associated with chain confinement.

### Self-avoiding chains

Figure 4 shows the phase behavior as a function of particle volume fraction for different values of particle-to-polymer size ratio when self-avoiding chains are connected to the colloids, and presents a quite different landscape. We still find that for sufficiently small  $\alpha$ , colloids crystallize into an FCC crystal by fitting the chains in the colloidal interstitial spaces (Fig. 4A). However, chains never mix to form vacancies, and as the length of the polymer increases, the colloidal crystal becomes frustrated and eventually ceases to form. Unlike the case of ideal polymers, we see no evidence of a micellar phase. We believe this is due to the large entropic barrier associated with overlapping multiple confined chains. This can be estimated by computing the confinement free energy of a polymer of length equal to the sum of all chains in the cavity, which would grow as  $\Delta F \propto (R_g^{\text{eff}}/R_m)^{3/(3\nu-1)}$ , where  $R_g^{\text{eff}}$  is the radius of gyration of a chain of length



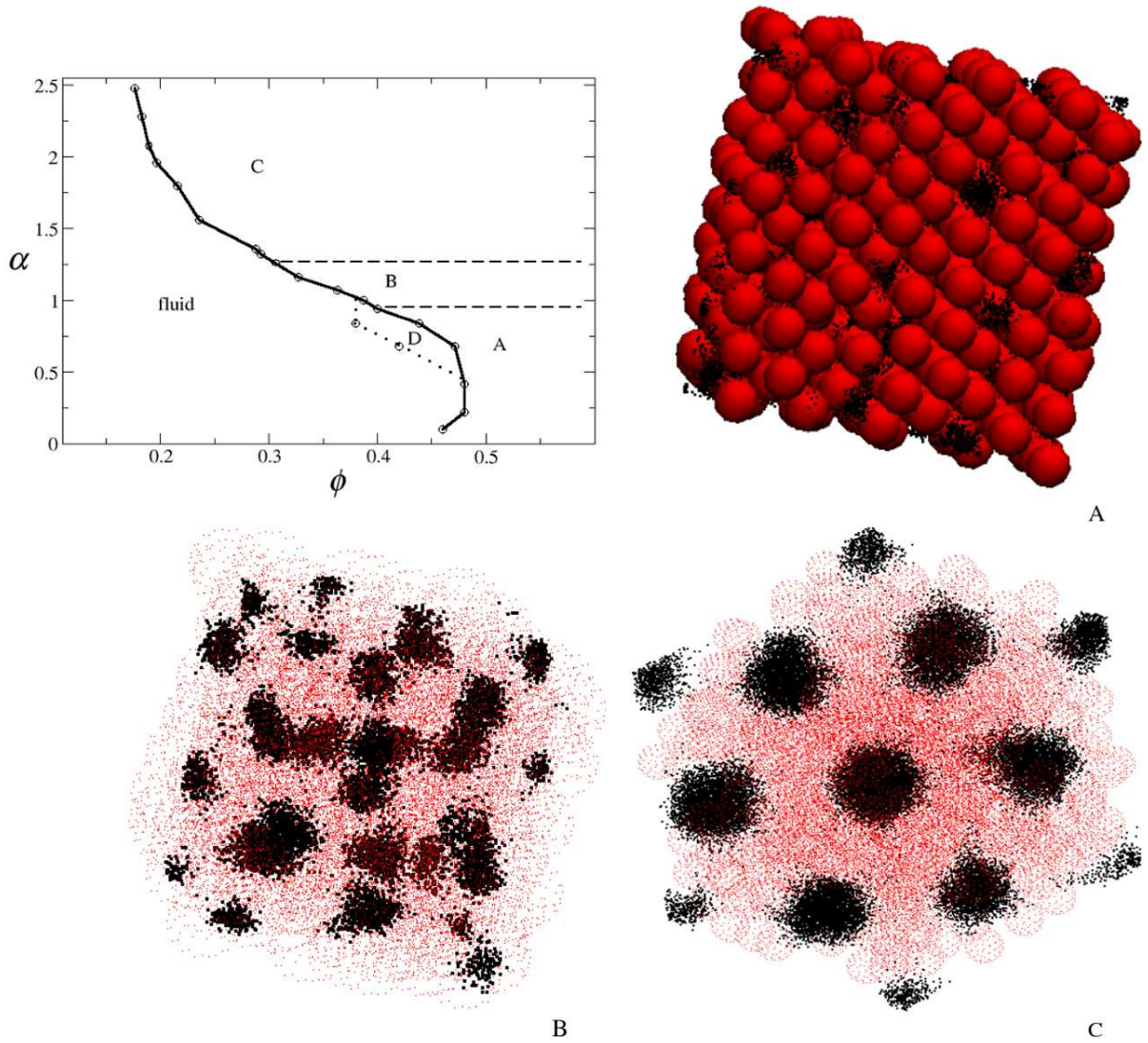


FIG. 2: (Color online) Phase diagram of colloids with ideal tethers as a function of the polymer-colloid size ratio  $\alpha$  and colloid volume fraction  $\phi$ . Snapshots of the phases in region (A), (B), and (C), depicting the colloidal crystal, the disordered micellar, and the micellar crystal phase, respectively, are also shown. For the sake of clarity, in snapshot (B) and (C), the colloidal particles are depicted using a light, low-density pixel representation, while the dark regions show where the polymer chains are located.

$nN$  and  $\nu \simeq 3/5$ . Clearly, the free energy dependence on both the number of chains  $n$  and size of the cage  $R_m$ ,  $\Delta F \propto n^{9/4}(R_g/R_m)^{3.75}$ , is much stronger than what obtained for ideal chains [27]. As a result, as soon as chains become confined, any significant amount of polymer overlap is highly unfavorable.

As the polymer size increases, for  $0.5 \leq \alpha \leq 1.75$ , the dense phase presents no colloidal order. Chains do not mix with each other and occupy the interstitial spaces in between colloids. The overall shape of the chains is elongated, as this geometry is entropically more favorable than a spherical one [28–30].

As soon as  $\alpha$  becomes larger than 1.75, the micellar phase found for ideal chains is replaced by a disordered bicontinuous phase (Fig. 4C), which allows for a more

effective lateral packing of the chains. This phase is preceded by the formation of small colloidal clusters driven together by a combination of depletion interactions and chain-chain repulsions (Fig. 4B). The colloid-rich region presents, in both cases, a significant degree of crystalline order.

The cluster phase is stable within a relatively narrow range of volume fractions, and is promptly transformed into the bicontinuous phase as soon as  $\phi$  is sufficiently large for the clusters to merge. Fig. 5 shows how the size of the largest colloidal cluster in the system, normalized by the total number of colloids, grows with the system volume fraction. It is worth mentioning that colloidal clusters can grow quite thick, and this can only be attained at the expense of the entropy of the polymers

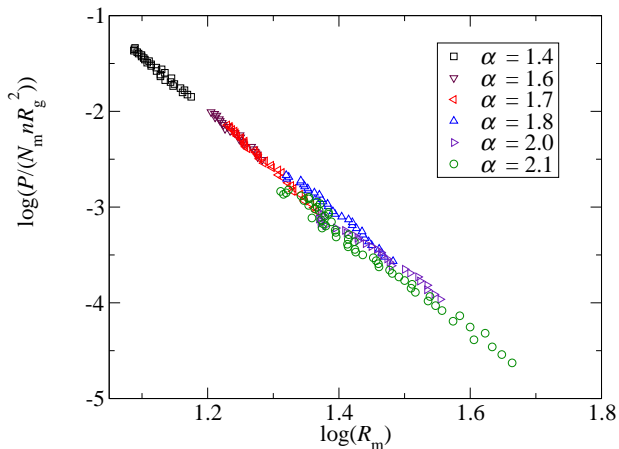


FIG. 3: (Color online) Data collapse of the rescaled pressure  $P/(N_m n R_g^2)$  as a function of micellar size  $R_m$  for different values of  $\alpha$ .

connected to the particles at the core of each cluster, as they need to be partially unwrapped. We believe that this free energy cost may actually limit the overall thickness of the clusters and incentivize linear, rather than isotropic, cluster growth.

The overall phenomenology in this region can again be understood in terms of chain confinement. It is well known [31] that the free energy cost to completely overlap two unconfined chains is about  $2k_B T$ , independent of the polymer length. As a result, at low volume fractions, there isn't a significant driving force for self-organization. However, as  $\phi$  increases and the chain sizes become smaller than  $R_g$ ,  $\Delta F$  acquires, as discussed above, a non-trivial dependence of the number of chains,  $n$ , sharing the same volume. This leads to chain reorganization and subsequent colloidal clustering. These clusters present no translational order or size monodispersity, and are stabilized by their mutual effective repulsions, which extend to a surface-to-surface range that is typically smaller than  $R_g$ . As soon as  $\phi$  is sufficiently large, clusters merge to further minimize chain-chain interactions and the bicontinuous phase discussed above is formed. For even larger volume fractions we observe significant ordering of the overall structure of the bicontinuous phase; however, the system sizes considered in this study are too small to make any conclusive claim in this regard.

The colloidal-cluster phase can be interpreted as a disordered inverted micellar phase. We cannot a priori exclude the existence of an inverted micellar crystal phase for even larger polymer lengths than the ones considered in this study, but such an analysis is out of the reach of our computational resources.

#### IV. CONCLUSIONS AND DISCUSSION

We report the phase behavior of a system of hybrid colloids formed by grafting a single polymer on the surface

of a colloidal particle. We find a variety of self-assembled structures as a function of polymer-colloid size ratio and volume fraction. The structures are driven by compressing the disordered low-density states and can be understood in terms of the entropy of both tethers and colloids. We have identified chain confinement as the key parameter to sort out the physical mechanisms driving self-assembly in this system.

It would be interesting to test whether, for self-avoiding polymers, an ordered bicontinuous phase and a crystal phase of inverted micelles can indeed be obtained, and to study how the phase behavior presented in this manuscript changes as a function of the number of grafted polymers.

We wish to stress that both disordered and ordered micellar phases were observed by Capone and collaborators [22] while studying a system of diblock copolymers modeled as an ideal and self-avoiding polymer with a density-dependent effective soft-sphere potential. This seems to suggest that (a) the nature of the micellar phase for ideal tethers is not too sensitive to the details of the interaction, and (b) for  $\alpha$  sufficiently large, ideal chains are indeed well-characterized by an additive effective pair potential. The problem becomes more complicated when dealing with self-avoiding polymers. When multiple polymers are confined within the same region their interaction energy does not scale linearly with the number of chains, but as  $n^{9/4}$ , and up to  $n^3$  for even larger densities [27]. This is clearly not pairwise additive. Some preliminary results obtained using an effective soft-spherical potential to describe the polymer (to be published elsewhere) indicate quite different phase behavior, including several ordered phases which are not found in our simulations with explicit polymers. This seems to suggest that a more sophisticated coarse-graining of self-avoiding polymers is required to obtain the correct phenomenological behavior of this system.

#### Acknowledgments

This work was supported by the National Science Foundation under CAREER Grant No. DMR-0846426.

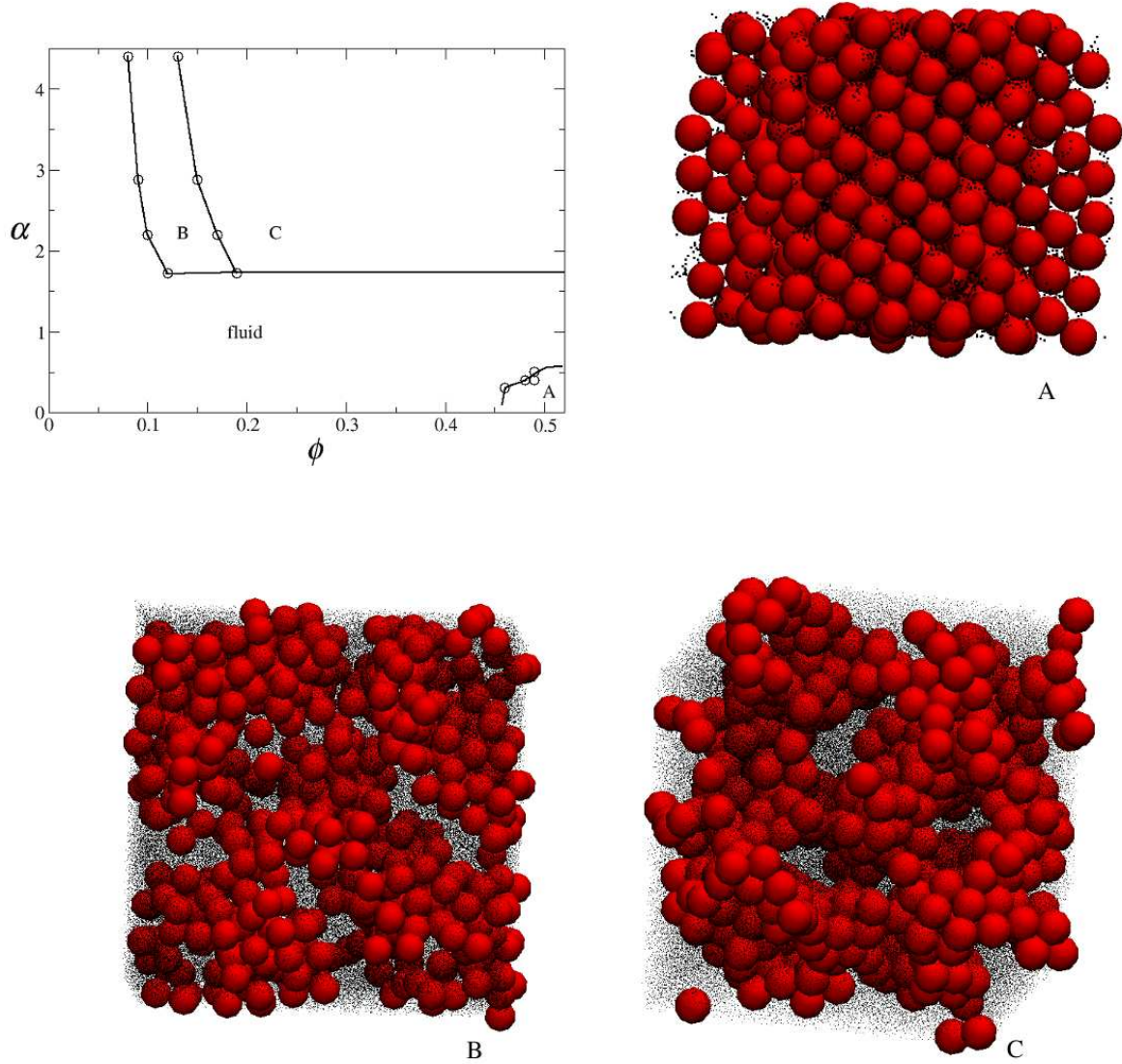


FIG. 4: (Color online) Phase behavior for the case of self-avoiding chains. In the graph in the top-left corner of the figure, the vertical axis indicates the polymer-colloid size ratio  $\alpha$  and the horizontal axis is the colloidal volume fraction  $\phi$ . Snapshots of the phases in region (A), (B) and (C), depicting the colloidal crystal, the colloidal cluster, and the bicontinuous phase respectively are also shown. For the sake of clarity, in snapshots (B) and (C), the polymers are depicted using a light, low density pixel representation.

- 
- [1] G.A. DeVries, *et al.*, Science **315**, 358 (2007).
  - [2] M. Li, H. Schnablegger, S. Mann, Nature **402**, 393 (1999).
  - [3] L. Hong, S. Jiang, S. Granick, Langmuir **22**, 9495 (2006).
  - [4] H. Weller, Phil. Trans. R. Soc. A **361**, 229 (2003).
  - [5] E. K. Hobbie *et al.*, Langmuir **21**, 10284 (2005).
  - [6] S. C. Glotzer and M. J. Solomon, Nature Materials **6**, 557 (2007).
  - [7] C. .R. Iacovella, M. A. Horsch, S. C. Glotzer, J. Chem. Phys. **129**, 044902 (2008).
  - [8] M. F. Hagan and D. Chandler, Biophys. J. **91**, 42 (2006).
  - [9] S. Whitlam and P.L. Geissler, J. Chem. Phys. **127**, 154101 (2007).

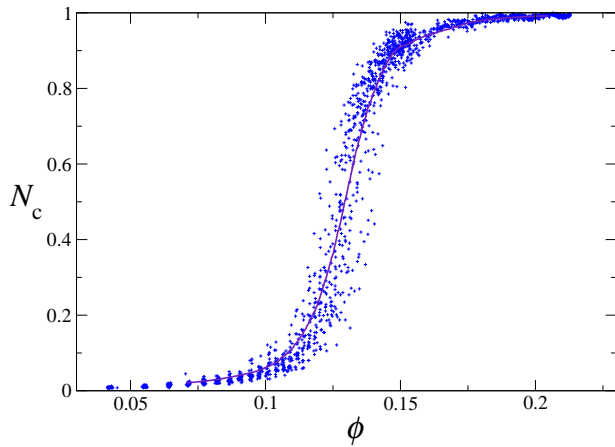


FIG. 5: Size of the largest colloidal cluster,  $N_c$ , (normalized by the total number of colloids) as a function of colloidal volume fraction,  $\phi$ , for self-avoiding tethers. Dots are simulations with colloids of size  $\sigma_2/\sigma_1 = 2.5$ , connected to  $N = 75$  monomers at different initial configurations. The solid line is a mobile average of the data points.

- [10] W. L. Miller and A. Cacciuto, *Phys. Rev. E* **80**, 021404 (2009).
- [11] S. Torquato, *Soft Matter* **5**, 1157 (2009).
- [12] P. Bolhuis and D. Frenkel, *J. Chem. Phys.* **106**, 666 (1997).
- [13] T. Chen, Z. L. Zhang, S. C. Glotzer, *Langmuir* **23**, 6598 (2007).
- [14] X. Zhang, Z. L. Zhang, S. C. Glotzer, *J. Phys. Chem. C* **111**, 4132 (2007).
- [15] B. S. John and F. A. Escobedo, *J. Phys. Chem. B* **109**, 23008, (2005).
- [16] T. Song, S. Dai, K. C. Tam, S. Y. Lee, and S. H. Goh, *Langmuir* **19**, 4798 (2003).
- [17] Y. Kim, J. Pyun, J. M. J. Fréchet, C. J. Hawker, and C. W. Frank, *Langmuir* **21**, 10444 (2005).
- [18] S. Westenhoff and N. A. Kotov, *J. Am. Chem. Soc.*, **124**, 2448 (2002).
- [19] D. Nykypanchuk, *et al.*, *Nature* **451**, 549 (2008).
- [20] S. Y. Park, *et al.*, *Nature* **451**, 553 (2008).
- [21] B. Bozorgui, D. Frenkel, *Phys. Rev. E Lett.* **101**, 045701 (2008).
- [22] B. Capone *et al.*, *J. Phys. Chem. B* **113**, 3629 (2008).
- [23] S. J. Plimpton, *J. Comp. Phys.* **117**, 1 (1995) <http://lammps.sandia.gov/index.html>
- [24] W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- [25] W. G. Hoover, *Phys. Rev. A* **34**, 2499 (1986).
- [26] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- [27] S. Jun and A. Arnold, *Phys. Rev. Lett.* **98**, 128303 (2007).
- [28] A. Cacciuto and E. Luijten, *Nano Lett.* **6**, 901 (2006).
- [29] T. Sakaue and E. Raphaël, *Macromolecules* **39**, 2621 (2006).
- [30] A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (American Institute of Physics, New York, NY, 1994).
- [31] P. G. Bolhuis, *et al.*, *J. Chem. Phys.* **114**, 4296 (2001).